

1000000000

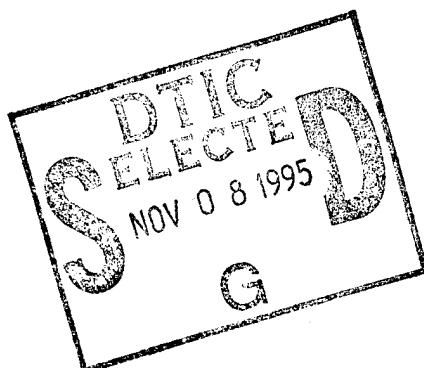
1000000000

122704

P-31

FINAL TECHNICAL REPORT

NASA Research Grant NAG-1-678



19951024 097

SPACE ENVIRONMENTAL EFFECTS ON POLYMERIC MATERIALS

May 1, 1986 to May 31, 1987

(NASA-CR-162454) SPACE ENVIRONMENTAL
EFFECTS ON POLYMERIC MATERIALS Final
Technical Report, 1 May 1986 - 31 May 1987
(College of William and Mary) 31 P CSCI 11B

N88-16879

Unclas
G3/27 0122994

Principal Investigators: RICHARD L. KIEFER
ROBERT A. ORWOLL

Grantee Institution: THE COLLEGE OF WILLIAM AND MARY
WILLIAMSBURG, VIRGINIA 23185

DEPARTMENT OF DEFENSE

RESEARCH, DEVELOPMENT, AND TEST REPORT

ARRADCOM, WUVA, 1000 0700

DISTRIBUTION STATEMENT A

Approved for public release;
Distribution Unlimited

5 DTIC QUALITY INSPECTED 5

PLASTED 517045

*MSG D14 DROLS PROCESSING-LAST INPUT IGNORED

-- 2 OF 6

DTIC DOES NOT HAVE THIS ITEM

-- 1 - A. NUMBER: D441845
-- 5 - CORPORATE AUTHOR: COLLEGE OF WILLIAM AND MARY WILLIAMSBURG VA
-- 6 - UNCLASSIFIED TITLE: SPACE ENVIRONMENTAL EFFECTS ON POLYMERIC
-- MATERIALS.
-- 9 - DESCRIPTIVE NOTE: FINAL TECH REPT., 86 MAY - 87 MAY
--10 - PERSONAL AUTHORS: KILFER, R. L.; ORWOLL, R. A.
--11 - REPORT DATE: MAY , 1986
--12 - PAGINATION: 30P
--15 - CONTRACT NUMBER: NAG-1-678
--18 - MONITOR ACRONYM: NASA
--19 - MONITOR SERIES: CR-182454
--20 - REPORT CLASSIFICATION: UNCLASSIFIED
--22 - LIMITATIONS (ALPHA): APPROVED FOR PUBLIC RELEASE; DISTRIBUTION
-- UNLIMITED. AVAILABILITY: NATIONAL TECHNICAL INFORMATION SERVICE,
-- SPRINGFIELD, VA. 22161.
- 33 - LIMITATION CODES: 1 24

-- END Y FOR NEXT ACCESSION

END

SPACE ENVIRONMENTAL EFFECTS ON POLYMERIC MATERIALS

Richard L. Kiefer and Robert A. Orwoll
 Department of Chemistry
 The College of William and Mary
 Williamsburg, VA 23185

Accession For	
NTIS CRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By _____	
Distribution /	
Availability Codes	
Dist	Avail and/or Special
A-1	•

ABSTRACT

Polymeric materials that may be exposed on spacecraft to the hostile environment beyond the earth's atmosphere have been subjected to atomic oxygen, electron bombardment, and ultraviolet radiation in terrestrial experiments.

Atomic Oxygen: Evidence is presented for the utility of an inexpensive asher for determining the relative susceptibility of organic polymers to atomic oxygen. Kapton, Ultem, P1700 polysulfone, and m-CBB/BIS-A (a specially formulated polymer prepared at NASA-Langley) all eroded at high rates, just as was observed in shuttle experiments.

Radiation: Films of Ultem, P1700 polysulfone, and m-CBB/BIS-A were irradiated with 85-keV electrons. The UV/VIS absorbance of Ultem was found to decay with time after irradiation indicating free radical decay. The tensile properties of Ultem began to change only after it had been exposed to 100 Mrads. The effects of dose rate, temperature, and simultaneous vs. sequential electron and UV irradiation were also studied.

INTRODUCTION

Polymeric materials are candidates for a variety of applications on orbiting space vehicles. Their use is planned, for example, in the matrix component in truss tube composites, in adhesives, in the substrate for large-area solar array panels, in thermal coatings, in paints that absorb stray light in orbiting telescopes, and in electrical insulation. However, these organic materials are vulnerable to the harsh environmental conditions found at orbital altitudes. High energy radiation, especially in the form of electrons and short-wavelength electromagnetic radiation, and atomic oxygen can have permanent, deleterious effects on these polymers. We have studied some of these effects in experiments that simulate some of the conditions in outer space. Our purpose has been to test a variety of polymeric materials to identify any that exhibit unusually high or low stability when subjected to radiation or atomic oxygen.

This report first describes studies of the effects on polymers of atomic oxygen, a very reactive substance that is an environmental hazard in low-earth orbit. Then we report on research with electron bombardment and ultraviolet radiation, both of which could be damaging to exposed organic polymers particularly in geosynchronous orbits.

ATOMIC OXYGEN - AN ENVIRONMENTAL HAZARD IN LOW-EARTH ORBIT¹

BACKGROUND

Atomic oxygen is formed in the earth's upper atmosphere by the photodissociation of diatomic oxygen, O_2 , and triatomic ozone, O_3 . Between ca. 200 and 700 km altitude, oxygen atoms are the most populous chemical species with concentrations varying between 10^{10} and 10^6 atoms/cm³.² Here it is found predominantly in its triplet ground state (3P) and two singlet excited states (1D and 1S). Atomic oxygen is an extraordinarily reactive

substance, both with other species and with itself. Consequently it cannot be stored for terrestrial experiments but must be generated in situ, thereby accounting in part for the paucity of studies involving atomic oxygen.

The possibility for degradation of polymeric materials at high altitudes was pointed out³ a number of years ago. However, only after Skylab and the first flights of the shuttle did it become widely recognized that organic materials on the exterior of vehicles in low-earth orbit would be susceptible to degradation by atomic oxygen. In the experiments that were performed on several shuttle missions, various materials were exposed to atomic oxygen. Included among them were a variety of polymer films, some coated with protective surfaces and others left uncoated. In the shuttle experiments, the speed of the vehicle (8 km/s) resulted both in high fluxes (typically 10^{13} - 10^{15} atoms/cm²sec) and in translational energies (5 eV corresponding to 40,000 K) far in excess of thermal energies.⁴

The shuttle experiments showed extensive etching of the forward-facing surfaces of unprotected organic films for those films that contained no elements other than carbon, hydrogen, oxygen, nitrogen, and sulfur.⁵ (In general metals are less susceptible than non-metals with the exception of silver and osmium.) Typically these films experienced average losses of 2 to 4 Å³⁶ for each impact with an atom of oxygen. At the fluxes encountered in low-earth orbit, this corresponds to an erosion of approximately 0.3 mm from a forward-facing surface over a 10-year period. The reactions with oxygen occur with little or no activation energy,⁷ thereby reducing the significance of the 5-eV collision energy. The rate of material loss seems to be almost independent of the temperature of the solid sample.^{8,9} Because the oxides of the constituent elements in these films are gases at ambient conditions, the reaction products of these elements with oxygen do not remain with the film. On the other hand, polymer films that have silicon atoms incorporated in their molecular formulation and the fluorocarbons TFE and FEP (both have the empirical formula CF₂) were found to be much

less susceptible to atomic oxygen.^{9,10,11} In the case of the silicon-containing polymers, the silicate oxidation products do not evaporate but remain behind, providing a protective coating on the film. The fluorinated polymers have a lower susceptibility to oxygen because they are already saturated with fluorine, the only element more electronegative than oxygen.

It was found that the vulnerable organic films can be protected from atomic oxygen by coating them with thin metallic, metal-oxide, silicon oxide, or fluorocarbon films^{8,12,13,14} or by incorporating additives⁶ that have high oxidative stability.

Carbon-epoxy and Kevlar-epoxy matrix composites also underwent erosion much like the unprotected organic films.^{10,15}

A variety of thin polymeric coatings applied to metal or metal oxide surfaces were studied in other shuttle experiments¹⁰. The qualitative results for the coatings were very similar to the results described above for films. Coatings that had polyurethane binders were among the most vulnerable to degradation by atomic oxygen. Photomicrographs showed the binder had eroded leaving behind particles of pigment material on the surface. On the other hand, coatings that had either a polydimethylsiloxane or a fluorocarbon base appeared to be very stable to attack by atomic oxygen.

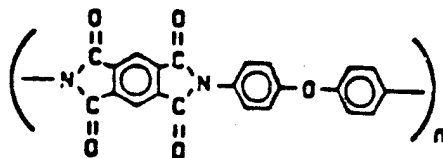
The effects of atomic oxygen on organic polymers have also been studied in terrestrial laboratories. Several methods have been used to generate oxygen atoms: an RF plasma generator or "asher"^{3,12,16,17}, a microwave resonant cavity with ionization and acceleration¹⁸, injection into high energy beams of rare gases or plasma^{19,20,21}, a DC arc-heated supersonic nozzle²², and a laser-sustained discharge,^{23,24} and reactive ion sputtering.^{16,25}

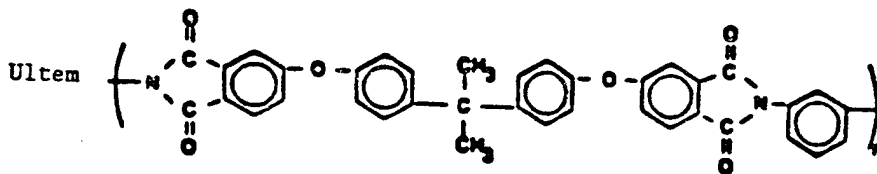
EXPERIMENTAL

Polymer films were exposed to atomic oxygen in the cavity of an RF plasma generator (SPI Plasma Prep II Model 11005) in the Applied Materials Branch at NASA-Langley. Molecular oxygen flowed into the chamber of this asher and was continuously dissociated by the electric field oscillating at 13.56 MHz. The pressure in the reaction chamber was maintained near 200 mTorr. The concentration of atomic oxygen was not determined. Samples of film to be used in the experiment were cut into thin disks with a diameter of 2.22 cm (7/8 inch) and mounted vertically on a Pyrex glass frame so that the flow of oxygen was approximately parallel to the flat surface of the disk. Three Pyrex U-tubes, placed in series between the outlet port of the plasma generator and the vacuum pump, were used to condense volatile products from the oxidation. They were connected to one another and to the rest of the system with stainless steel (Cajon) joints so that they could be removed individually. In the trapping experiments the first U-tube downstream from the sample was cooled to -78°C with a Dry Ice/acetone bath while the next two traps were maintained at -196°C using liquid nitrogen.

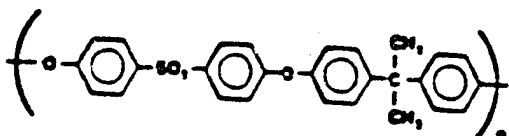
The polymers studied in this series of experiments included the polyimides Kapton H (du Pont) and Ultem (General Electric), P1700 polysulfone (Union Carbide) and a polyarylene ether which was formulated and prepared in the Polymeric Materials Branch at NASA-Langley.²⁶ The last polymer is referred to as m-CBB/BIS-A. The molecular structures are drawn here.

Kapton

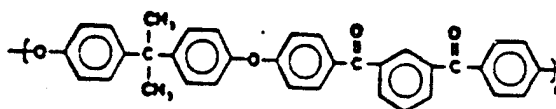




P1700



m-CBB/BIS-A



For the first three polymers, commercially prepared films were used. The polyarylene ether studies used films that had been drawn from 10-20% solutions of polymer in dimethylacetamide.

RESULTS

1. Mass Loss Measurements

Each of the four polymer samples was subjected to atomic oxygen for a measured period of time, removed from the plasma generator, weighed in air, returned to the generator, and the cycle repeated. Because the results were dependent on the position and orientation of the sample in the chamber, special care was taken to load the samples in the chamber in the same way for each run. The mass of each sample decreased at an almost uniform rate with little difference among the different polymers. For the 22-mm-diameter films, all values fell in the range 5.7 to 8.4 mg/hr for weighings made every 30 min over a 5-hr period. Kapton was found to have the smallest erosion rate, and m-CBB/BIS-A the greatest. These values correspond to erosion rates of ca. 15 to 25 Å/s from the surfaces of the film. This is

very close to the value of 29 Å/s found³ for a "polyimide" in a similar study with an asher operating at the higher pressure of 1 Torr. For comparison, these polymers on the shuttle experiments⁶ eroded at a rate of 0.010 Å/s when they were situated in a ram-facing position under typical orbital conditions (i. e., a surface flux of oxygen atoms of 3.5×10^{13} /cm²s); that is, a one-second exposure to oxygen in the asher corresponds to about a half hour at these orbital conditions.

Other mass-loss studies were made on these same four polymers. However, instead of removing the samples from the chamber at frequent intervals for weighing, we kept previously unexposed films in the atomic oxygen for long periods without interruption before finally weighing them in the ambient conditions of the laboratory. In these experiments the erosion rates increased by 10-50%. While the reason for this is not clear, it may be a consequence of adsorption of water or other atmospheric component onto the fresh surfaces of the films when they were removed from the chambers for the periodic weighings. This coating would provide a temporary protective layer for the film in the subsequent treatment with oxygen. Another possible explanation for the differences in mass loss is that any free radicals that may have been formed near the surface during exposure and contributed to the degradation are destroyed when the sample is exposed to air.

2. Product Collection

Mechanisms proposed for the reaction of atomic oxygen with organic polymers predict the initial formation of species that are incompletely oxidized.^{3,17,27,28} In the hope that finding such compounds, we condensed the gaseous products that were being exhausted from the reaction chamber during long-term (7-8 hr) exposures to atomic oxygen. However, the only products found were water, carbon dioxide, sulfur dioxide (in the experiments with the polysulfone), and nitrogen dioxide (in the experiments with the polyimide Kapton). Products were found only in the first two U-tubes

(maintained at -78° and -196°C); the third tube in the sequence (also at -196°C) remained empty.

The products collected in the U-tubes were analyzed in several ways. In one set of experiments the U-tubes were allowed to come to room temperature and then were rinsed with small amounts of one of the following solvents: dichloromethane, chloroform, sec-butanol, carbon tetrachloride, and acetone. A sample of the rinse was injected into a gas chromatograph (gc) equipped with a capillary column and flame-ionization detector. No solute was detected by gc. The species that are gases at room temperature are not sufficiently soluble in the solvents to be revealed in this gc experiment, and the gc detector is insensitive to water. However, water was detected in the washings of the first tube with sec-butanol when the washings were analyzed with infrared spectroscopy (IR).

The most volatile contents of the U-tubes were transferred as gases into an IR gas cell. Infrared analysis of the -196°C condensate in the middle of the three tubes showed carbon dioxide from each of the four polymers. Nitrogen dioxide (NO_2) was found to be an oxidation product of Kapton when the contents of the middle U-tube were analyzed by gas-phase IR spectroscopy. Similarly, sulfur dioxide (SO_2) was observed in experiments with Pl700 polysulfone. The middle U-tube was not analyzed when Ultem was treated with atomic oxygen, and, consequently, no oxidation product of nitrogen was seen for this polymer. Presumably it is also NO_2 . No products other than CO_2 , NO_2 , and SO_2 were detected in any of the gas-phase IR experiments. While it is likely that incompletely oxidized species may have been present near the surface of the film, they would have undergone additional reactions with oxygen between the target and the cold traps.

CONCLUSIONS

In these experiments with the RF plasma generator, the polyarylene ether, the polysulfone, and the two polyimides suffered mass losses in

atomic oxygen that did not differ significantly one from another. This mirrors in a qualitative way the observations made in studies in orbit on the Shuttle. Experiments performed³ many years ago with a similar earth-bound plasma generator showed a somewhat greater spread in reactivities for hydrocarbon polymers. Unlike the present work, these studies included polymers that have no aromaticity and therefore have a greater reactivity with oxygen. As in the shuttle experiments, these same earlier laboratory studies³ found that the completely fluorinated hydrocarbons TFE and FEP have a much greater resistance to oxygen. The results of other experiments^{12,16,17} with ashers have also been consistent with the findings from low-earth orbit in determining the relative ranking of resistances to atomic oxygen. Thus we conclude that the simple RF plasma generator is a valuable device even though it does not accurately reproduce such orbital conditions as the 5-eV impact energy of atomic oxygen, the distribution of oxygen atoms among the possible quantum states, the charges that the oxygen and/or target¹⁶ may carry, the oxygen flux, and the concurrent bombardment by high-energy radiation.

In a continuation of this work we will use this technique to identify additives for high performance polymers that will reduce their sensitivity to atomic oxygen and render them more useful for spacecraft applications.

ELECTRON AND ULTRAVIOLET RADIATIONS

BACKGROUND

There are two major orbits into which space vehicles are launched: the Low Earth Orbit (LEO), and the Geosynchronous Earth Orbit (GEO). Both orbits lie above the protective ozone layer, thus objects in either orbit are subjected to a flux of 1.4 Kw/m^2 of solar ultraviolet radiation²⁹. In addition, the Geosynchronous Earth Orbit lies at the edge of the outer Van

Allen radiation belt so that objects in this region are subjected to energetic electrons and protons (0.1 to 4 MeV) each with a flux of $10^8 \text{ cm}^{-2} \text{ sec}^{-1}$.²⁹ Over a 30-year lifetime, a composite material in the GEO will have an absorbed dose of approximately 10^{10} rads. This dose level exceeds the threshold for damage in most polymer systems studied.³⁰ Radiation is known to initiate chain scission and crosslinking in polymeric materials, both of which affect their structural properties. Thus, studies of the effect of ionizing radiation on polymers is important in estimating the impact of the space environment on structures made of composite materials.

EXPERIMENTAL

Four different experiments were performed to investigate various aspects of the interaction of ionizing radiation with polymeric materials. The experiments are described separately below.

1. Effect of Exposure to Air after Irradiation

The polyetherimide, Ultem, which has been described above, darkens with irradiation, a characteristic common to many polymer films. However, when Ultem is exposed to air after irradiation, the color fades. To quantify this color change, ultraviolet/visible (UV/VIS) spectra of irradiated Ultem films were recorded at various times after irradiation beginning at 5 minutes and extending to at least 4 hours. The spectra were recorded on a Perkin-Elmer 330 spectrophotometer. Films of Ultem with a thickness of 76 microns (3 mil) were irradiated in vacuum with 85 KeV electrons to total doses of 100, 320, 640, 2000, and 4000 Mrads. Dose rates ranged from 4.2 to 170 Mrads/hr.

As indicated below, the color change in Ultem film is probably caused by radicals. Thus, the fading of the color is likely accompanied by a decay of one or more radical species. To test the effect of this radical density

on mechanical properties, tensile elongation measurements were made on 1/2 inch strips of the irradiated Ultem film with an Instron model TT-M1. Since each tensile elongation test required 30 to 40 minutes, irradiated films were removed from the vacuum chamber and immediately immersed in liquid nitrogen. Individual films were then removed and exposed to air for a prescribed time before the test was made. Time periods of 0, 15, 30, 60, and 120 minutes of air exposure were used.

2. Effect of Dose Rate

To achieve the 30-year dose of 10^{10} rads in some reasonable time, dose rates much higher than that experienced in GEO must be used. When studying radiation effects on materials, it is important to know whether these higher dose rates affect the results. To investigate the effect of dose rate on the mechanical properties, a study was carried out using a polysulfone, P1700, which is described above. This polymer was chosen because it had been well characterized, it was available commercially in good quality films, measurable radiation effects could be achieved with moderate doses and previous studies showed that it did not become lighter in color on exposure to air after irradiation. P1700 films 76 microns thick were irradiated in vacuum with 85 KeV electrons to a constant total dose of 350 Mrads at a constant temperature of 25°C. Irradiations were performed under these conditions with dose rates of 1.8, 4.9, 7.3, 20.6, 87.5, and 263 Mrads/hr. Mechanical properties were monitored with tensile elongation measurements using an Instron model TT-M1.

3. Effect of Temperature During Irradiation

During each orbital period a structure in Earth orbit is subjected to large temperature changes. Thus, it is important to know how the temperature of a material effects the damage done by ionizing radiation. In this study, 76 micron P1700 film was irradiated in vacuum with 85 KeV electrons. All irradiations were performed with a constant dose rate of 87.5 Mrads/hr

to a constant total dose of 350 Mrads. The temperature of the film in the irradiation chamber was controlled by mounting the film firmly against a steel plate through which oil at a specified temperature was circulated. The temperature of the film was monitored with a thermocouple positioned between the film and the plate. Irradiations were carried out with film at temperatures of 25, 50, 75, 100, 110, 125, 150, and 175°C. For all irradiations, the films remained in vacuum until they were cooled to room temperature.

4. Simultaneous and Sequential Irradiations with Electrons and UV Radiation

Structures in the GEO are subjected to simultaneous irradiation with charged particles and ultraviolet radiation. Most radiation damage studies deal with one or the other of these radiations separately, or at best with both radiations sequentially. It is important to know if there is a synergistic effect with simultaneous irradiation. A unique instrument at the NASA Langley Research Center allows materials to be irradiated simultaneously with electrons up to 100 KeV and ultraviolet radiation with intensities up to 5 suns. In addition, volatile products can be monitored during irradiation with a built-in mass spectrometer.

Studies of simultaneous and sequential irradiations were carried out with films of m-CBB/BIS-A. The structure of this material is shown above on page 6. Films of the polymer about 50 microns (2 mil) in thickness were irradiated with 85 KeV electrons at a dose rate of 9.4 Mrads/hr, and ultraviolet radiation from a xenon lamp at an intensity of 1.5 suns. In the sequential studies, films were irradiated for 5 consecutive days with one radiation, followed by 5 consecutive days with the other. For the simultaneous studies, films were irradiated for five consecutive days with both radiations. Immediately after all irradiations, ultraviolet/visible spectra of the films were recorded with a Perkin-Elmer Model 330 spectrophotometer. A second spectrum was taken after the films were exposed to air for 24

hours. Baseline spectra were also recorded before the start of irradiation in all cases.

RESULTS

1. Effect of Exposure to Air After Irradiation

The ultraviolet/visible spectra of the irradiated Ultem films were taken 5 minutes after the irradiated film was exposed to air and continued at various times up to 4 hours. All spectra were stored by the instrument and subsequently plotted on the same graph to show the change in % transmittance with exposure to air. Figure 1 shows the results for an Ultem film exposed to a total dose of 4000 Mrads. Preliminary experiments showed that further changes did not occur in the UV/VIS spectrum after 4 hours of air exposure. The plot to the far right in Figure 1 is the spectrum of the unirradiated material, which is nearly colorless. The spectrum with the lowest %T was taken after 5 minutes of air exposure. Subsequent spectra show a progressively higher %T, indicating that the absorption in the visible region decreases, and the color of the film fades with increased time of air exposure. In Figure 2, the %T at 490 nm is plotted against time of exposure to air for films irradiated to two different total doses. It can be seen that the %T increased with time of air exposure up to a maximum value which was always less than that of the unirradiated film. To investigate further the decrease in color, the %T at each exposure time was subtracted from the maximum or equilibrium value. The logarithm of this remainder is plotted as a function of exposure time in Figure 3. This plot shows the decay of the color and thus the decay of the species causing the color. Two distinct groups of points are evident in Figure 3; those from films irradiated to high doses (2000 and 4000 Mrads), and those from films irradiated to lower doses (320 and 640 Mrads). The color of the films irradiated to high doses decayed with a half-life of 90 minutes, while that of the films irradiated to lower doses decayed with a 40 minute half-life. It has been shown by ESR spectroscopy that for an Ultem film irradiated to

1600 Mrads, the radicals decay with a 90 minute half-life.³¹ This constitutes good evidence that the decay of the color centers is due to radical decay. It has also been shown that the critical gel dose for Ultem is about 1100 Mrads.³² Thus, it is possible that above the critical gel dose, the radicals decay more slowly due to a decrease in mobility or to a change in decay mechanism. The UV/VIS data as a function of total dose is summarized in Figure 4. It can be seen that color changes in Ultem film do not occur until a dose of 100 Mrads is reached.

Tensile elongation measurements also showed no onset of effects until a dose of 100 Mrads was reached. These data are plotted in Figure 5, where the similarity with Figure 4 is readily apparent. Since the effect of radiation on tensile elongation followed qualitatively with the color darkening, studies were made to test the effect of exposure to air on the mechanical properties. Measurements were made at various air exposure times from 0 to 120 minutes. The data plotted in Figure 6, show that within experimental uncertainty, there is no effect of air exposure on the tensile elongation. In addition, two samples were irradiated to 350 Mrads and allowed to remain in vacuum for 4 days before making tensile elongation measurements as a function of exposure time in air. Again no effect was noted. Tensile elongation data for Ultem film irradiated to several different doses is summarized in Figure 7.

2. Effect of Dose Rate

Preliminary experiments had shown that films of the polysulfone, P1700, were not as radiation resistant as films of Ultem. Thus, measurable radiation effects could be achieved with moderate radiation doses. Furthermore, after irradiation P1700 does not become lighter in color with exposure to air. This behavior is shown in Figure 8 where UV/VIS spectra of irradiated P1700 taken 5 minutes to 4 hours after irradiation are plotted. It can be seen that the spectra show little change in absorption over the time period. This can be compared to Figure 1 where similar data are plotted for Ultem.

The results of the dose rate studies are shown in Figure 9. Over the range of dose rates studied (1.8 to 263 Mrads/hr), there is no effect on the tensile elongation for P1700 film. At all dose rates, the tensile elongation was about 80% of that for the unirradiated material.

3. Effect of Temperature During Irradiation

Films of P1700 were irradiated at various temperatures to a constant dose of 350 Mrads at a constant dose rate of 87.5 Mrads/hr. Tensile elongation measurements for the irradiated films are plotted as a function of temperature in Figure 10. Between 110 and 125°C the tensile elongation drops from about 100% to 0. The probable reason for this dramatic change is that the critical gel dose decreases with increasing temperature. Within this range of temperatures, the critical gel dose falls below 350 Mrads and thus the polymer film shows a sudden embrittlement. Brown and O'Donnell have shown that for gamma-ray irradiation of P1700, the critical gel dose decreased from 400 Mrads at 35°C to 100 Mrads at 125°C.³³ This is qualitatively in line with our data. There also appears to be a slight increase in tensile elongation as the temperature increases from 25 to 110°C. It has been shown for P1700 that the ratio of chain scission to crosslinking, $G(S)/G(X)$, increases with increasing temperature.³³ This would cause an increase in tensile elongation with increasing temperature up to the point where the critical gel dose is exceeded.

4. Simultaneous and Sequential Irradiations with Electrons and UV Radiation

A preliminary examination of the data indicates that at the levels of radiation used, much more effect is seen from the ultraviolet radiation than from the electron bombardment. This may simply be due to the difference in the amount of energy incident on the film from each source. Qualitatively, it also appears that there is no difference between simultaneous and sequential irradiations. A quantitative analysis of the data is currently

underway. No volatile products could be observed during the irradiations on the m-CBB/BIS-A films.

Conclusions

For studies using Ultem film, post-irradiation handling is important for optical properties, but appears to have no effect on the tensile elongation. Polysulfone P1700 film shows little or no effect of post-irradiation handling on its optical properties. In both polymers, radiation causes an irreversible color change. Initially, the Ultem becomes darker than P1700, however, its color fades over a period of 3 to 4 hours to a permanent color more nearly that of the other material.

The polysulfone, P1700, shows no effect of dose rate on its mechanical properties over the range studied. However, the lowest dose rate (1.8 Mrads/hr) is still about 40 times higher than the dose rate in the GEO. The value of 1.8 Mrads/hr represented the smallest rate at which the electron gun could be run in a stable condition.

The temperature at which P1700 is irradiated definitely affects the mechanical properties. Above 110°C, the polymer becomes completely brittle when irradiated to 350 Mrads. Below this temperature, the polymer film elongates to almost 100% of its original length. In the GEO, temperatures could vary between -100 and +100°C. In this study, no irradiations were carried out at temperatures below 25°C. Future experiments at lower temperatures would be valuable.

Quantitative analysis of the data from the simultaneous and sequential irradiations is being performed. The results could be important in interpreting experiments where only one radiation was used.

REFERENCES

1. Much of the research reported in this section was carried out by Daniel P. Gianturco, a William and Mary student: Daniel P. Gianturco, "Effect of Atomic Oxygen Exposure on Organic Polymers," Senior Honors Thesis, College of William and Mary, April 1987.
2. D. R. Peplinski, G. S. Arnold, and E. N. Borson, "Introduction to: Simulation of Upper Atmosphere Oxygen. Satellite Exposure to Atomic Oxygen in Low Earth Orbit," 13th Space Simulation Conference, NASA Conference Publication 2340, October 1984, p. 133.
3. R. H. Hansen, J. V. Pascale, T. de Benedictis, and P. M. Rentzepis, "Effect of Atomic Oxygen on Polymers," J. Polym. Sci., Part A, 3, 2205 (1965).
4. L. Leger, B. Santos-Mason, J. Visentine, and J. Kuminecz, "Review of LEO Flight Experiments," Proceedings of the NASA Workshop on Atomic-Oxygen Effects, J.P.L. Publication 87-14, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, June 1987, p. 1.
5. J. T. Visentine, L. J. Leger, J. F. Kuminecz, and I. K. Spiker, "STS-8 Atomic Oxygen Effects Experiment," AIAA 23rd Aerospace Sciences Meeting, AIAA-85-0415, January 1985.
6. L. J. Leger, "Effects of the Low Earth Orbital Environment on Spacecraft Materials," Proceedings of the Third European Symposium on Spacecraft Materials in Space Environment, Noordwijk, The Netherlands, October 1985.
7. J. C. Gregory and P. N. Peters, "The Production of Glow Precursors by Oxidative Erosion of Spacecraft Surfaces," 2nd Workshop on Spacecraft Glow, NASA Conference Publication 2391, 1985, p. 174.
8. P. Fraundorf, D. Lindstrom, N. Pailer, S. Sandford, P. Swan, R. Walker, and E. Zinner, "Erosion of Mylar and Protection by Thin Metal Films," AIAA Shuttle Environment and Operations Meeting, AIAA-83-2636, October 1983.
9. L. J. Leger, I. K. Spiker, J. F. Kuminecz, T. J. Ballentine, and J. T. Visentine, "STS Flight 5 LEO Effects Experiment--Background Description and Thin Film Results," AIAA Shuttle Environment and Operations Meeting, AIAA-83-2631-CP, October 1983.

10. W. S. Slemp, B. Santos-Mason, G. F. Sykes, Jr., and W. G. Witte, Jr., "Effects of STS-8 Atomic Oxygen Exposure on Composites and Coatings," AIAA 23rd Aerospace Sciences Meeting, AIAA-85-0421, January 1985.
11. L. Leger, J. Visentine, and B. Santos-Mason, "Selected Materials Issues Associated with Space Station," SAMPE Quarterly, 18, 48 (1987).
12. B. A. Banks, M. J. Mirtich, S. K. Rutledge, D. M. Swec, and H. K. Nahra, "Ion Beam Sputter-Deposited Thin Film Coatings for Protection of Spacecraft Polymers in Low Earth Orbit," AIAA 23rd Aerospace Sciences Meeting, AIAA-86-4428, January 1985.
13. K. A. Smith, "Evaluation of Oxygen Interaction with Materials (EOIM) - STS-8 Atomic Oxygen Effects," AIAA-86-14404, 1986.
14. A. F. Whitaker, J. A. Burka, J. E. Coston, I. Dalins, S. A. Little, R. F. DeHaye, "Protective Coatings for Atomic Oxygen Susceptible Spacecraft Materials - STS-41G Results," AIAA-86-14400, 1986.
15. D. G. Zimcik, "Advanced Composite Materials Exposure to Space Environment (ACOMEX) on STS 41-G," Can. Aero. Space J., 31, 249 (1985), AIAA-86-22999; D.G. Zimcik and C. R. Maag, "Results of Apparent Atomic Oxygen Reactions with Spacecraft Materials during Shuttle Flight STS-41G," AIAA-86-14403.
16. A. Garton, F. D. McLean, W. Wiebe, and R. J. Densley, "Exposure to Cross-linked Epoxy Resins to the Space Environment," J. Appl. Polym. Sci., 32, 3941 (1986).
17. P. W. Knopf, R. J. Martin, R. E. Damman, and M. McCargo, "Correlation of Laboratory and Flight Data for the Effects of Atomic Oxygen on Polymeric Materials," AIAA 20th Thermophysics Conference, AIAA-85-1066, June 1985.
18. D. C. Ferguson, "The Energy Dependence and Surface Morphology of Kapton Degradation under Atomic Oxygen Bombardment," 13th Space Simulation Conference, NASA Conference Publication 2340, October 1984, p. 205.
19. A. Freedman, W. Unkel, J. Silver, and C. Kolb, "Hypervelocity Supersonic Nozzle Beam Source of Atomic Oxygen," 13th Space Simulation Conference, NASA Conference Publication 2340, October 1984, p. 146.

20. P. Mahadevan, "Atomic Beam System for Laboratory Simulation of Upper Atmospheric Oxygen Atom Impact on STS Surfaces," 13th Space Simulation Conference, NASA Conference Publication 2340, October 1984, p. 222.
21. R. C. Tennyson, J. B. French, L. J. Kok, and J. Kleiman, "An Atomic Oxygen Facility for Studying Polymer Materials for Spacecraft Applications," 13th Space Simulation Conference, NASA Conference Publication 2340, October 1984, p. 169.
22. G. S. Arnold and D. R. Peplinski, "A Facility for Investigating Interactions of Energetic Atomic Oxygen with Solids," 13th Space Simulation Conference, NASA Conference Publication 2340, October 1984, p. 150.
23. J. B. Cross, "A Low Earth Orbit Molecular Beam Space Simulation Facility," 13th Space Simulation Conference, NASA Conference Publication 2340, October 1984, p. 193; J. B. Cross, D. A. Cremers, and D. F. Tucker, "Ground-Based Investigations of Atomic Oxygen Interactions with Space Station Surfaces," AIAA 20th Thermophysics Conference, AIAA-85-1068, June 1985.
24. J. B. Cross, L. H. Spangler, M. A. Hoffbauer, F. A. Archuleta, L. Leger, and J. Visentine, "High Intensity 5 eV Atomic Oxygen Source and Low Earth Orbit Simulation Facility," Proceedings of the NASA Workshop on Atomic Oxygen Effects, J.P.L. Publication 87-14, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, June 1987, p. 105.
25. R. A. Ferrieri, Y. Y. Chu, and A. P. Wolf, "A Sputtering Derived Atomic Oxygen Source for Studying Fast Atom Reactions," Proceedings of the NASA Workshop on Atomic Oxygen Effects, J.P.L. Publication 87-14, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, June 1987, p. 119.
26. P. M. Hergenrother, B. J. Jensen, and S. J. Havens, "Poly(arylene ethers) from Bis-1,3 and 1,4-(4-chlorobenzoyl)benzene," Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem., 26, 174 (1985).
27. D. R. Coulter, R. H. Liang, S. Y. Chung, K. O. Smith, and A. Gupta, "O-Atom Degradation Mechanisms of Materials," Proceedings of the NASA Workshop on Atomic-Oxygen Effects, J.P.L. Publication 87-14, Jet Propulsion

Laboratory, California Institute of Technology, Pasadena, CA, June 1987, p. 39.

28. R. J. Cvetanovic, "Kinetics and Mechanisms of Some Atomic Oxygen Reactions," Proceedings of the NASA Workshop on Atomic-Oxygen Effects, J.P.L. Publication 87-14, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, June 1987, p. 47.

29. D. R. Tenney, G. F. Sykes, Jr., and D. E. Bowles, "Space Environmental Effects on Materials," AGARD Conference Proceedings, 1983, AGARD-CP-327, June 1983.

30. J. F. Kircher and R. E. Bowman, Effects of Radiation on Materials and Components, Reinhold, New York, 1964.

31. E.R. Long and S.A.T. Long, "Spectroscopic Analysis of Radiation-Generated Changes in Tensile Properties of Polyetherimide Film," NASA TP-2429, May 1985.

32. R. Basheer and M. Dole, "The Radiation Chemistry of Polyetherimides," Radiat. Phys. Chem., 25, 389 (1985).

33. J.R. Brown and J.H. O'Donnell, "Effects of Gamma Radiation on Two Aromatic Polysulfones. II. A Comparison of Irradiation at Various Temperatures in Air-Vacuum Environments," J. Appl. Polym. Sci., 23, 2763 (1979).

Polyetherimide
UV/VIS Spectra

4000 Mrads

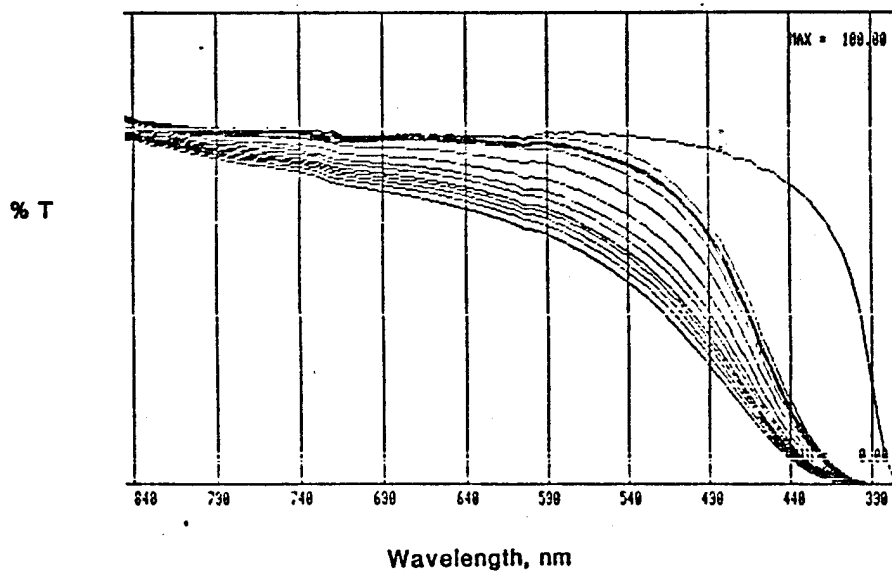


Figure 1. UV/VIS spectra of Ultem taken 5 minutes to 4 hours after irradiation.

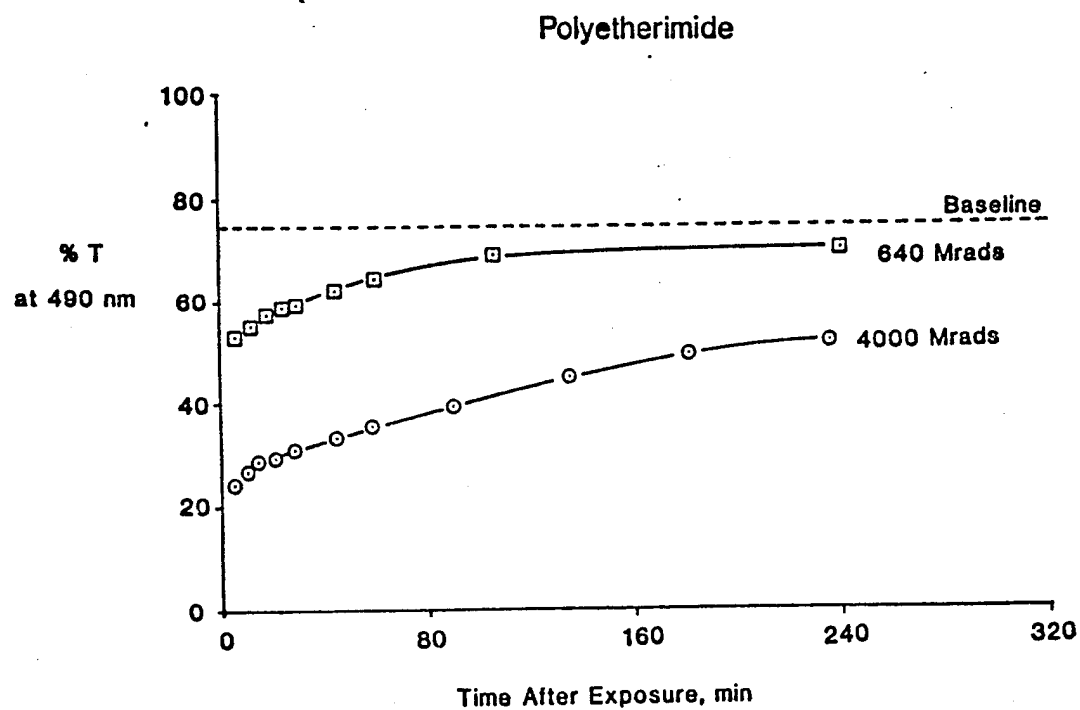


Figure 2. Percent transmittance at 490 nm of irradiated Ultem as a function of time after irradiation.

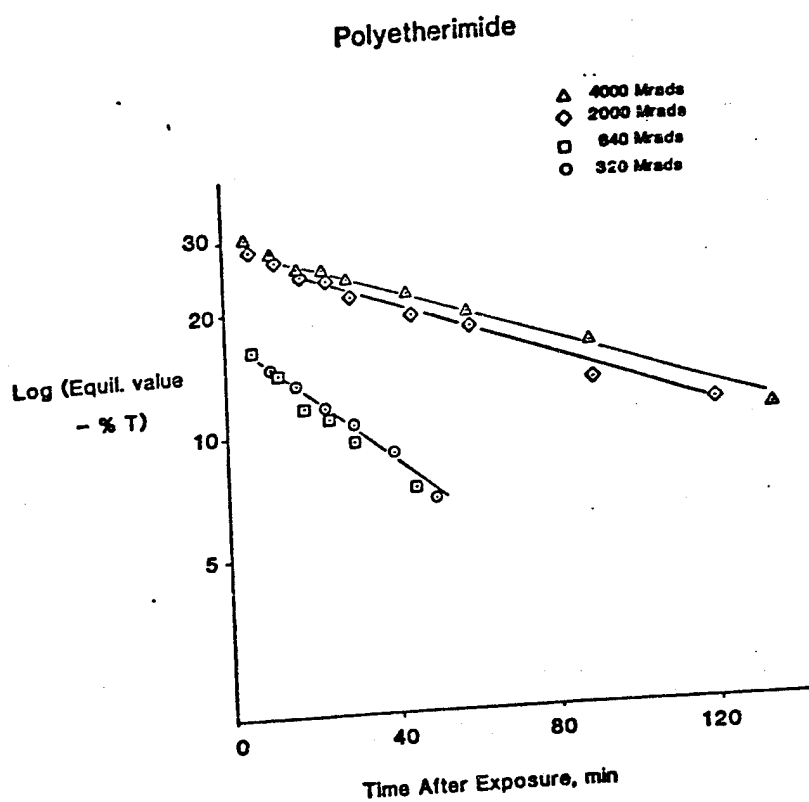


Figure 3. The decay of the color centers of irradiated Ultem.

Polyetherimide

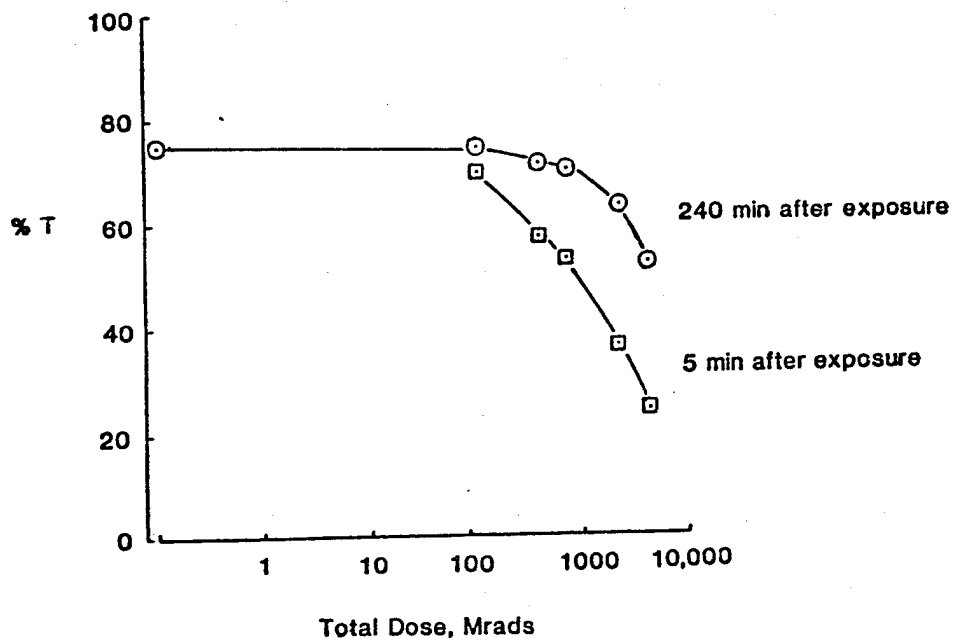


Figure 4. Percent transmittance of irradiated Ultem as a function of total dose.

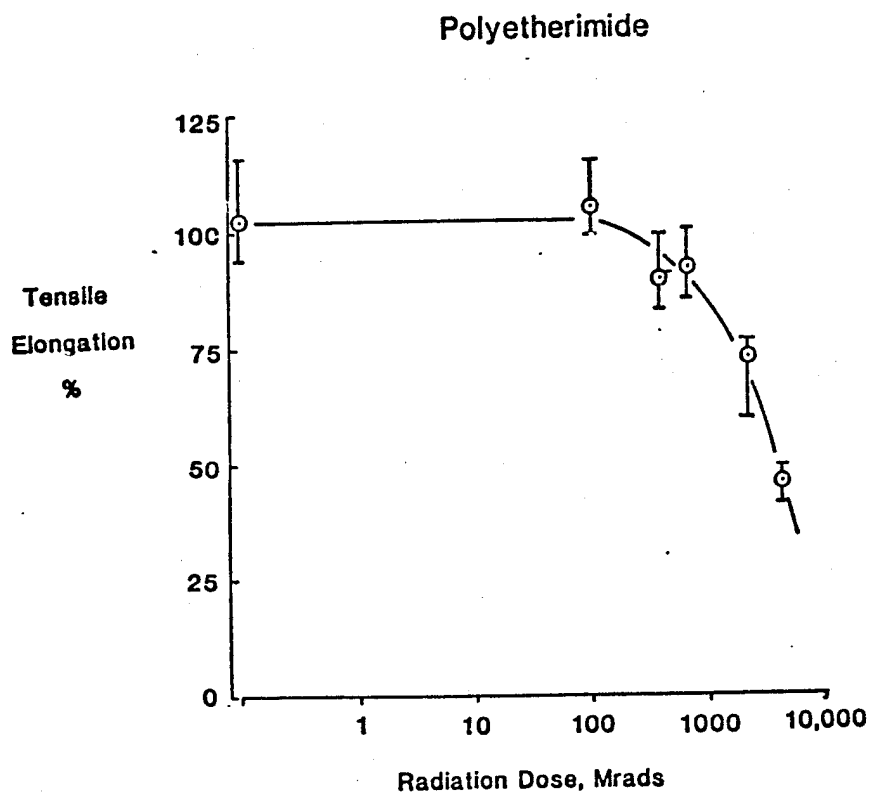


Figure 5. Tensile elongation of irradiated Ultem as a function of total dose.

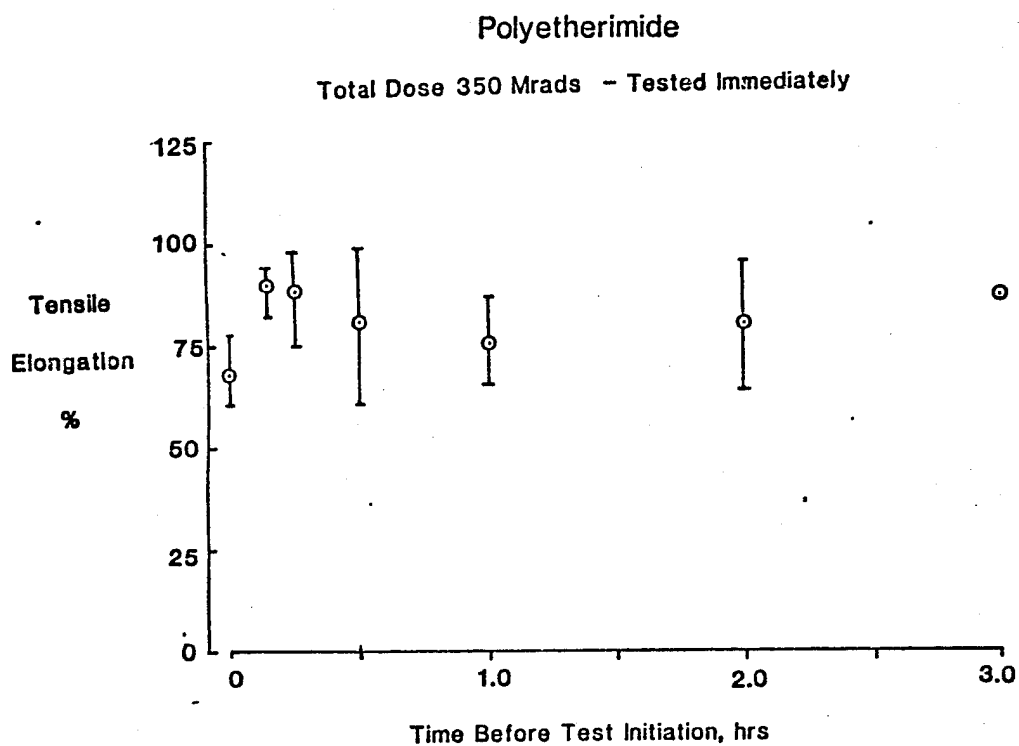


Figure 6. Tensile elongation of irradiated Ultem as a function of exposure time in air.

Polyetherimide

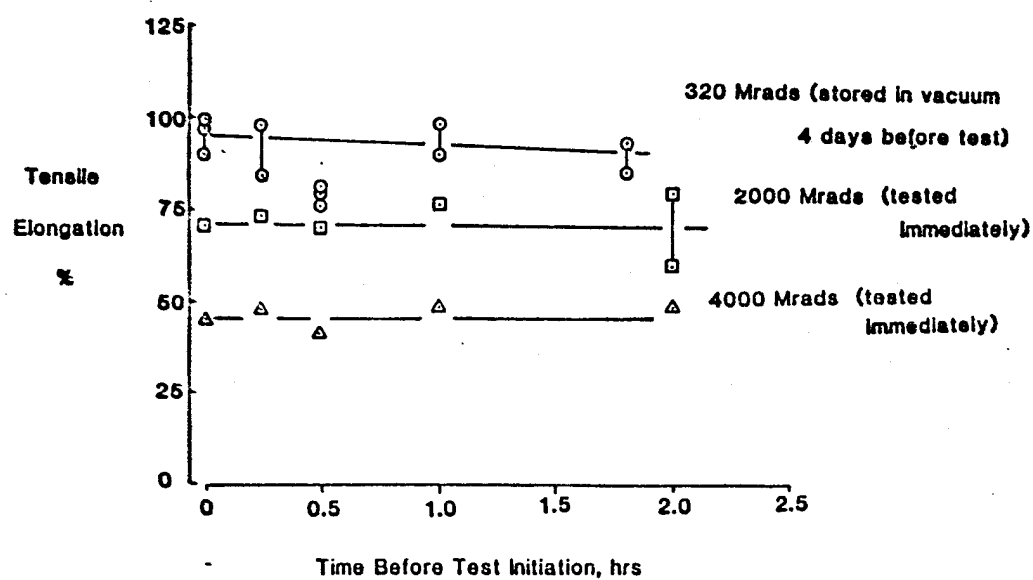


Figure 7. Tensile elongation of Ultem irradiated to various doses as a function of exposure time in air.

Polysulfone
UV/VIS Spectra

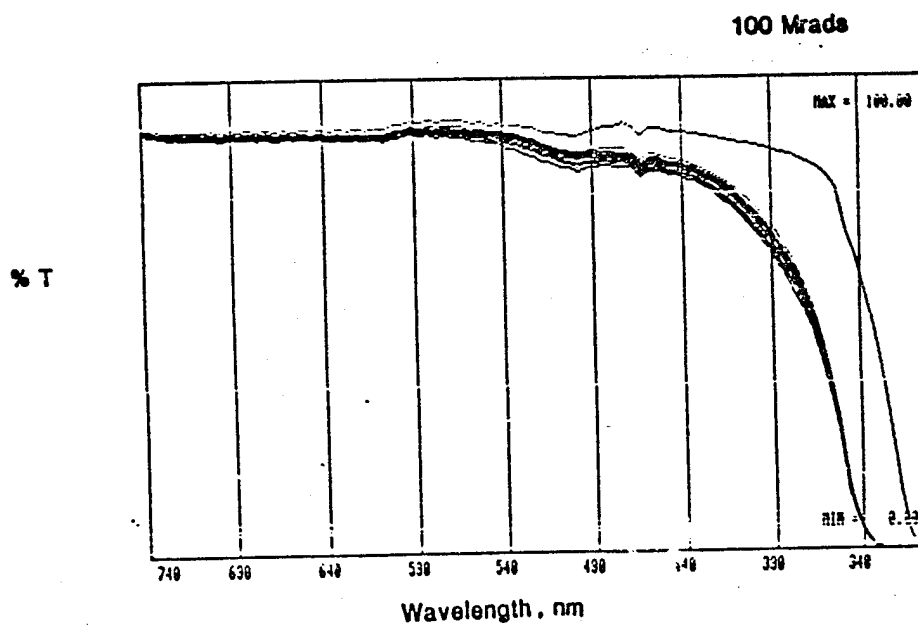


Figure 8. UV/VIS spectra of polysulfone taken 5 minutes to 4 hours after irradiation.

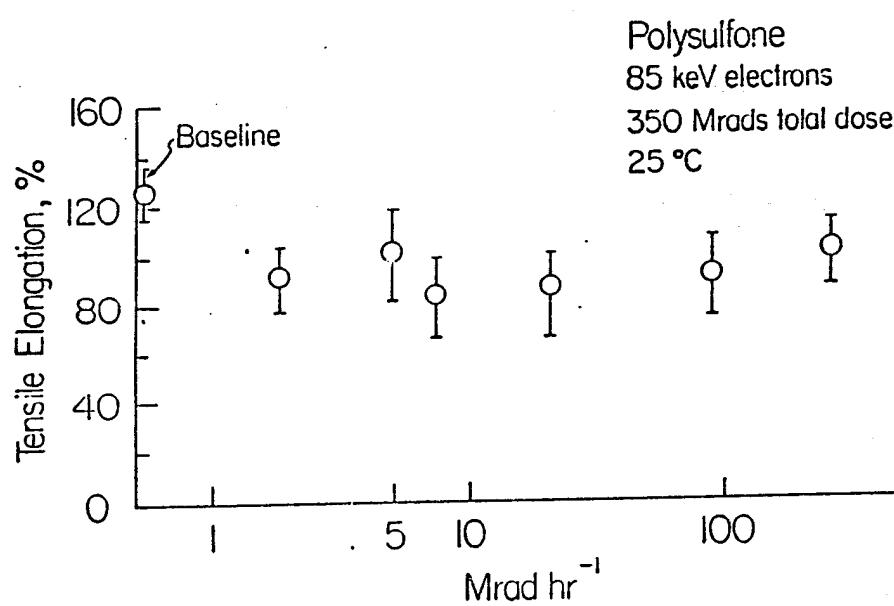


Figure 9. Tensile elongation of polysulfone as a function of dose rate.

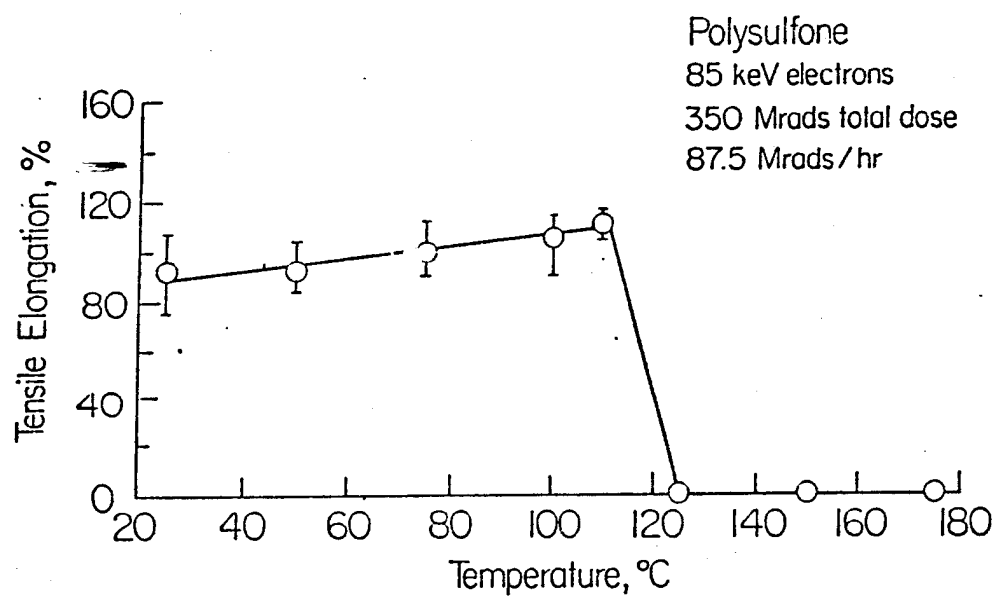


Figure 10. Tensile elongation of polysulfone as a function of temperature.